The hyperfine structure of the hydrogen molecular ion*

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Abstract

Theoretical investigations of the hyperfine structure of the hydrogen molecular ion (one electron and two protons) are discussed. The nuclear spin-rotation interaction has been found to be of the same sign as in the hydrogen molecule and the hyperfine transition frequencies can be accurately predicted. With measurements of the hyperfine structure of the deuterium molecular ion (or of HD$^+$) it should be possible to obtain a value of the deuteron quadrupole moment that could be compared with the values obtained from the deuterium molecule and from nuclear theory.

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INTRODUCTION

The calculation of hyperfine structure (hfs) frequencies presents a substantial challenge to theory, in part because the experimental spectroscopic data available are so precise. For the hydrogen atom in the $1s$ state, with electron spin $S = \frac{1}{2}$ and nuclear spin $I = \frac{1}{2}$, the transition frequency between the $F = 0$ and $F = 1$ states, where $\mathbf{F} = \mathbf{I} + \mathbf{S}$, is known to be $1\,420.405\,751\,766\,7(9)$ MHz [1], in comparison to the most complete theoretical result of $1\,420.405\,1(8)$MHz [2], which includes reduced mass, QED, and hadronic (mainly proton recoil and size) effects. Indeed, a simple "Fermi" theory of the hfs (see, for example, [3], p. 74) with a fixed proton and the electron and proton g-factors of, respectively, $2.002\,319$ and $5.585\,694$, gives about $1\,422$ MHz and with the correction due to the reduced mass of the proton-electron system it yields $1\,420.5$ MHz. Further inclusion of the known QED corrections yields a value of about $1\,420.452$ MHz [4] and an additional ~ -45 kHz and the theoretical error comes from hadronic effects [2]. Needless to say, the difficulty of the calculations increases substantially at each stage [5].

The "hydrogen atom" of molecular physics is the hydrogen molecular ion H_2^+ consisting of two protons bound by a single electron. From a theoretical point of view this molecule offers a good starting point for investigations of molecular hfs since the electronic wave function can be calculated to high accuracy. Surprisingly, there have been only a few experiments on the hfs of H_2^+ [6–8], one experiment on HD^+ [9,10] , and no experiments on D_2^+.

With the deuterated ions it should be possible to determine the electric quadrupole moment of the deuteron, once the hfs transition energies are measured, and a further discussion of the prospects of using D_2^+ to do this will be given below.

THEORY OF H_2^+ HFS

As with the hydrogen atom, the hfs in H_2^+ arises primarily from interactions between the electron spin and nuclear spin, but there are also smaller magnetic effects arising from the electron and nuclear spins interacting with the magnetic field of the rotating nucleus.

The hfs energy can be described by the effective spin Hamiltonian

$$H_{\text{hfs}} = b\mathbf{I} \cdot \mathbf{S} + cI_zS_z + d\mathbf{S} \cdot \mathbf{N} + f\mathbf{I} \cdot \mathbf{N}, \tag{1}$$

where $\mathbf{I}$, $\mathbf{S}$, and $\mathbf{N}$ are, respectively, the total nuclear spin, electron spin, and rotational angular momenta, and b, c, d, and f are the coupling constants. Transition frequencies are obtained by diagonalizing the matrix elements of (1) with constants calculated from theoretical expressions or if given measured frequencies the constants can be determined by fitting using matrix elements of (1); usually the $b_{\beta S}$ [11] angular momentum coupling scheme is used in which the intermediate vector $\mathbf{F}_2 = \mathbf{I} + \mathbf{S}$ is formed, and then the total $\mathbf{F} = \mathbf{F}_2 + \mathbf{N}$.

Early theoretical studies of H_2^+ hfs were motivated by a need for predictions of transition frequencies of the $N = 1$ rotational level of the $v = 0$ vibrational state for astrophysical searches (it is now believed that there is little prospect for detection, cf. [12]), because no experimental data were available. The researchers calculated coupling constants and transition frequencies using (1) with $f = 0$. Transition frequencies were estimated by Burke [13]

using calculations of b, c, and d, and by Mizushima [14] who used values of b and c calculated by Stephens and Auffray [15]. A significant advance in the theory was the derivation by Dalgarno, Patterson, and Somerville [16] of the b, c, and d terms of (1) from the Dirac eq for H_2^+ by a nonrelativistic reduction within the Breit-Pauli approximation. They demonstrated that d could be written $d = d_1 + d_2$, where d_1 is the electron spin-rotational magnetic interaction and d_2 is a second-order term in the electronic wave function. They calculated values for b, c, and d_1, estimated d_2, and calculated transition frequencies and the constants b and c were used by Richardson, Jefferts, and Dehmelt to make the first experimental estimate of d [6]. Further improvements in calculations of b, c, and d_1, and improved estimates of d_2 were presented by Somerville [17,18] and by Luke [19]. The second-order constant d_2 was calculated accurately using a variation-perturbation method by Kalaghan and Dalgarno [20] and by McEachran, Veenstra, and Cohen [21], who also calculated b, c, and d_1 and accurate transition frequencies.

The calculated constants discussed so far were all determined in the Born-Oppenheimer approximation in which the electron is assumed to move in the field generated by averaging over the electronic wave function. Nonadiabatic effects on the ground electronic state through the excitation of other electronic states due to the coupling of electronic and nuclear motion contribute significantly to the constant b and the effects of the reduced mass of the electron on the constants have been treated [22,23].

The nuclear spin-rotation term f was introduced into the effective spin Hamiltonian (1) on phenomenological grounds by Jefferts [7], who measured the hfs transition frequencies for the $v = 4$–8 vibrational states. For the $N = 1$ rotational level for each v, he obtained values of the constants by fitting to (1). Varshalovich and Sannikov [12] obtained different fits to Jefferts' data, notably, they found the value of f to be negative. The first (and to date the only) measurements of the hfs of the $N = 1$ level of $v = 0$ state were carried out by Fu, Hessels, and Lundeen [8] through spectroscopy of high angular momentum Rydberg states of the hydrogen molecule H_2 and by fitting the measured Rydberg transition levels to an effective spin Hamiltonian including (1) they determined values for b, c, d, and f.

A recent theoretical study of the nuclear spin-rotation interaction in H_2^+ found the sign of f to be negative [24]. The nuclear spin-rotation interaction can be written

$$f(R) = f_1(R) + f_2(R), \tag{2}$$

and the major contributions [25] to the energy hf are from the interaction of each nuclear magnetic moment with the magnetic field generated by the other rotating nucleus,

$$hf_1(R) = -\frac{4g_p\mu_N^2}{R^3}, \tag{3}$$

and with the magnetic field generated by the orbiting electron [26],

$$hf_2(R) = -\frac{12g_p\mu_N^2}{\alpha^2 R^2}\sigma_{\text{hf}}(R), \tag{4}$$

where in atomic units R is the internuclear distance, μ_N is the nuclear magneton, and the dimensionless quantities α, g_p, and σ_{hf} are, respectively, the fs constant, the proton g-factor defined previously, and the high-frequency component of the magnetic shielding constant as defined in Eq. (3) of [24].

In Table I values of the hfs constants calculated as in [23] and the nuclear spin-rotation constants calculated as in [24], averaged over the vibrational wave functions, are compared with constants measured [8] for the $N = 1$ level of the $v = 0$ state and with constants determined [12] from the measurements [7] on the $N = 1$ level of the vibrational state $v = 4$. The agreement between theory and experiment is impressive—the theoretical constants in Table I reproduce all measured transition frequencies to within 175 kHz. The formalism of [23] accounts for reduced mass effects on the hfs constants but not fully for radiative and relativistic effects.

DEUTERON MOLECULAR ION

The electric quadrupole moment Q of the deuteron can serve as a sensitive test of models of the neutron-proton nuclear force [27]. The most accurate determination $Q = 0.2860 \pm 0.0015 \times 10^{-26} \text{cm}^2$ was obtained semiempirically from measurements [28] of the magnetic hfs of the deuterium molecule D_2 through a theoretical value for the electric field gradient at the nucleus due to the other constituent charges of the molecule [29,30]. It should be possible to measure Q semiempirically using D_2^+, which has the theoretical advantage of a simpler electronic structure than D_2, thereby facilitating accurate computation, but to date there have been no measurements of the hfs of D_2^+. (An experiment that measured hfs levels of HD^+ was reported, but the quadrupole effects were not resolved [9].)

For D_2^+, the effective spin Hamiltonian is (1) plus an additional nuclear quadrupole interaction [31] proportional to eqQ, where e is the proton charge and q is the electric field gradient. Predictions of the hfs constants and electric quadrupole coupling constant for the $N = 1$ level of the $v = 0$ state of D_2^+ are given in Table II. The constants b, c, and d have been calculated as in [23] with the inclusion of nonadiabatic effects in b and c, and f has been calculated using the theory of [24]. The term eqQ was estimated by calculating q in the Born-Oppenheimer approximation and using the semi-empirical value of Q from D_2. More detailed calculations of the hfs constants, quadrupole coupling constants, and transition frequencies will be reported [32].

The quadrupole coupling constant is about 57 kHz, see Table II. The experimental precision achieved in the ion trap experiments on H_2^+ was better than 3 kHz [7], in the Rydberg H_2 experiment it was around 20 kHz [8], and in a laser-rf double-resonance ion beam study of N_2^+ it was better than 10 kHz [33]. It would appear that the prospects are good for measuring the deuteron quadrupole moment using D_2^+.

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REFERENCES

[1] H. Hellwig, R. F. C. Vessot, M. W. Levine, P. W. Zitzewitz, D. W. Allan, and D. J. Glaze, IEEE Trans. Instrum. **IM-19**, 200 (1970).

[2] J. Sapirstein, in *Atomic Physics 14*, No. 323 in *AIP Conference Proceedings*, edited by D. J. Wineland, C. E. Wieman, and S. J. Smith (American Institute of Physics, New York, 1995).

[3] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1990).

[4] J. Sapirstein and D. Yennie, in *Quantum Electrodynamics*, edited by T. Kinoshita (World Scientific, Singapore, 1990), p. 560.

[5] J. M. Jauch and F. Rohrlich, *The theory of photons and electrons: the relativistic quantum field theory of charged particles with spin one-half* (Springer-Verlag, New York, 1976), pp. 531–2.

[6] C. B. Richardson, K. B. Jefferts, and H. G. Dehmelt, Phys. Rev. **165**, 80 (1968).

[7] K. B. Jefferts, Phys. Rev. Lett. **23**, 1476 (1969).

[8] Z. W. Fu, E. A. Hessels, and S. R. Lundeen, Phys. Rev. A **46**, R5313 (1992).

[9] W. H. Wing, G. A. Ruff, W. E. Lamb Jr., and J. J. Spezeski, Phys. Rev. Lett. **36**, 1488 (1976).

[10] There have been measurements of hfs in highly-excited vibrational states of HD$^+$ carried out by Carrington and collaborators, cf. A. Carrington, I. R. McNab, and C. A. Montgomerie, J. Phys. B **22**, 3551 (1989), but the present paper is concerned with the low-lying vibrational states for which hyperfine levels have been measured most accurately.

[11] R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

[12] D. A. Varshalovich and A. V. Sannikov, Astron. Lett. **19**, 290 (1993).

[13] B. F. Burke, Ap. J. **132**, 514 (1960).

[14] M. Mizushima, Ap. J. **132**, 493 (1960).

[15] M. J. Stephen and J. P. Auffray, J. Chem. Phys. **31**, 1329 (1959).

[16] A. Dalgarno, T. N. L. Patterson, and W. B. Somerville, Proc. Roy. Soc. London **259A**, 100 (1960).

[17] W. B. Somerville, Mon. Not. R. Astr. Soc. **139**, 163 (1968).

[18] W. B. Somerville, Mon. Not. R. Astr. Soc. **147**, 201 (1970).

[19] S. K. Luke, Ap. J. **156**, 761 (1969).

[20] P. M. Kalaghan and A. Dalgarno, Phys. Lett. **38A**, 485 (1972).

[21] R. P. McEachran, C. J. Veenstra, and M. Cohen, Chem. Phys. Lett. **59**, 275 (1978).

[22] J. F. Babb and A. Dalgarno, Phys. Rev. Lett. **66**, 880 (1991).

[23] J. F. Babb and A. Dalgarno, Phys. Rev. A **46**, R5317 (1992).

[24] J. F. Babb, Phys. Rev. Lett. **75**, 4377 (1995).

[25] Ref. [3], pp. 162–166, 208–213.

[26] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

[27] M. A. Preston and R. K. Bhaduri, *Structure of the nucleus* (Addison-Wesley, Reading, Massachusetts, 1975), pp. 123–130.

[28] R. F. Code and N. F. Ramsey, Phys. Rev. A **4**, 1945 (1971).

[29] R. V. Reid Jr. and M. L. Vaida, Phys. Rev. Lett. **34**, 1064 (1975), errata.

[30] D. M. Bishop and L. M. Cheung, Phys. Rev. A **20**, 381 (1979).

[31] C. H. Townes and A. L. Schawlow, *Microwave spectroscopy* (McGraw-Hill, New York, 1955), Chap. 6.

[32] J. F. Babb and A. Dalgarno, in preparation.

[33] N. Berrah Mansour, C. Kurtz, T. C. Steimle, G. L. Goodman, L. Young, T. J. Scholl, S. D. Rosner, and R. A. Holt, Phys. Rev. A **44**, 4418 (1991).

TABLES

TABLE I. Comparison of H_2^+ hfs constants from theory with those obtained from experimental measurements of hfs levels, for the $N = 1$ rotational levels of the $v = 0$ and $v = 4$ vibrational states. All values are given in MHz and numbers in parenthesis represent errors quoted on the last digit.

	b	c	d	f	Ref.
Theory, $v = 0$	880.163	128.482	42.421	−0.042	[23,24]
Experiment, $v = 0$	880.187(22)	128.259(26)	42.348(29)	−0.003(15)	[8]
Theory, $v = 4$	804.104	98.008	32.658	−0.036	[23,24]
Experiment, $v = 4$	804.087(2)	97.930(2)	32.649(2)	−0.034(2)	[12]

TABLE II. Predictions of the hfs constants and the electric quadrupole coupling constant for the molecular ion D_2^+ in the $N = 1$ rotational state of the $v = 0$ vibrational level. All values are given in MHz.

b	c	d	f	eqQ
135.739	19.944	21.461	−0.002	0.057